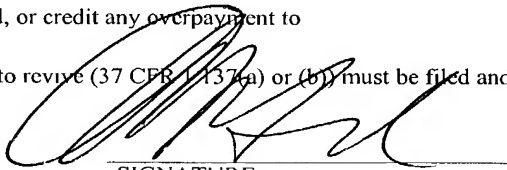


11. Assignee: AMTEC MAGNETICS GMBH of Ludwigshafen, GERMANY
12. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
13. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
14. ☒ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☒ Figure of Drawing to be published 1
18. ☒ Other items or information:
Cover Sheet and International Application as published(in German).
PCT/IPEA/416(in German).
PCT/IPEA/409(in German).
PCT/ISA/210(in German and English).
Cover Letter under 35 U.S.C. 371 and 1.495.
Claim of Priority.

| | | | | | |
|--|--------------|--|------------|------------------------------------|----|
| U.S. APPLICATION NO (If known, see 37 CFR 1.5) <div style="font-size: 1.5em; font-weight: bold;">10/031933</div> | | INTERNATIONAL APPLICATION NO PCT/EP00/06766 | | ATTORNEY'S DOCKET NUMBER P21955 | |
| 19. <input checked="" type="checkbox"/> The following fees are submitted <div style="margin-left: 20px;"> Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search report has been prepared by the EPO or JPO. \$ 890.00 International preliminary examination fee paid to USPTO (37 CFR 1.482). \$ 710.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO(37 CFR 1.445(a)(2)). \$ 740.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO. \$1,040.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4). \$ 100.00 ENTER APPROPRIATE BASIC FEE AMOUNT = </div> | | | | CALCULATIONS PTO USE ONLY | |
| Surcharge of \$130.00 for furnishing the oath or declaration later than ____ 20 ____ 30 months from the earliest claimed priority date (37 CFR 1.492(e)). | | | | \$ | |
| Claims | Number Filed | Number Extra | RATE | | |
| Total Claims | 20 - 20 = | 0 | X \$18.00 | \$0.00 | |
| Independent Claims | 1 - 3 = | 0 | X \$84.00 | \$0.00 | |
| Multiple dependent claim(s) (if applicable) | | | + \$280.00 | \$ | |
| TOTAL OF ABOVE CALCULATIONS = | | | | \$890.00 | |
| ____ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. | | | | \$ | |
| SUBTOTAL = | | | | \$890.00 | |
| Processing fee of \$130.00 for furnishing the English translation later than ____ 20 ____ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). | | | | + | |
| Extension of Time fee in the amount of \$ | | | | | |
| TOTAL NATIONAL FEE = | | | | \$890.00 | |
| Fee for recording the enclosed assignment (37 CFR 1.21(h) The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property | | | | + | |
| TOTAL FEES ENCLOSED = | | | | \$890.00 | |
| | | | | Amount to be refunded | \$ |
| | | | | Charged | \$ |
| a. <input checked="" type="checkbox"/> A check in the amount of \$890.00 to cover the above fees is enclosed. b. ____ Please charge my Deposit Account No. ____ in the amount of \$____ to cover the above fees. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 19-0089. NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.437(a) or (b)) must be filed and granted to restore the application to pending status. <div style="display: flex; justify-content: space-between;"> <div style="width: 40%;"> SEND ALL CORRESPONDENCE TO CUSTOMER NO. 7055 AT THE PRESENT ADDRESS OF: Neil F. Greenblum GREENBLUM & BERNSTEIN, P L C. 1941 Roland Clarke Place Reston, VA 20191 (703) 716-1191 </div> <div style="width: 20%; text-align: center;">  <div style="font-size: 1.5em; font-weight: bold;">07055</div> PATENT TRADEMARK OFFICE </div> <div style="width: 35%; text-align: right;">  SIGNATURE Neil F. Greenblum NAME <div style="font-size: 1.2em;">Reg. No. 33,099</div> 28,394 REGISTRATION NUMBER </div> </div> | | | | | |

P21955.A02

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Claudius KORMANN
Group Art Unit: Unknown
Appl. No. : Not Yet Assigned (National Stage of PCT/EP00/06766)
Examiner: Unknown
I.A. Filed : July 15, 2000
For : LITHIUM INTERCALATION COMPOUNDS
CONTAINING LITHIUM MANGANESE OXIDE

PRELIMINARY AMENDMENT

Assistant Commissioner of Patents
Washington, D.C. 20231

Sir:

Prior to calculation of the filing fees and examination of the above-identified patent application, entry of the following amendment is respectfully requested.

IN THE CLAIMS

Please amend claims 3-7, 11, 14 and 16, as follows (a marked-up copy of the changes is attached in an Appendix to the present amendment):

3. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 and 2] claim 1, where the specific BET surface area is from 0.5 to 1.9 m²/g.

4. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 and 2] claim 1, where the specific BET surface area is from 0.6 to 1.5 m²/g.

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5. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 to 4] claim 1, where the particle size, determined from the d_{50} value, is greater than $1\ \mu\text{m}$.

6. (Amended) A lithium intercalation compound having a spinel structure and containing lithium manganese oxide as claimed in [claims 1 to 5] claim 1, where the diameter, determined from the d_{90} value, is less than $25\ \mu\text{m}$.

7. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 to 5] claim 1, where the diameter, determined from the d_{90} value, is less than $20\ \mu\text{m}$.

11. (Amended) A process for the preparation of a lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 8 to 10] claim 8, where the particulate, crystalline spinel precursor compound consists of the three phases MnO , LiMnO_2 and Mn_3O_4 .

14. (Amended) A process as claimed in [one of claims 8 to 13] claim 8, where, after the heating in an oxidizing atmosphere, the resultant solid is suspended in water with addition of one or more alkaline lithium compounds, and the suspension is spray-dried at a temperature of from 100°C to 400°C .

16. (Amended) A process as claimed in [one of claims 8 to 15] claim 8, where the intimate mixing is carried out in the presence of a sintering aid in a concentration of from 0.1 to 3%, based on the weight of the solids employed.

[illegible]

P21955.A02

REMARKS

The Examiner is respectfully requested to enter the foregoing amendment to remove multiple dependent claims prior to examination of the above-identified patent application.

The amendments to the claims made in this amendment have not been made to overcome the prior art, and thus, should be considered to have been made for a purpose unrelated to patentability, and no estoppel should be deemed to attach thereto.

Should there be any questions, the Examiner is invited to contact the undersigned at the below-listed telephone number.

Respectfully submitted,
Claudius KORMANN

Neil F. Greenblum
Reg. No. 28,394

Ref No. 33,094

January 25, 2002
GREENBLUM & BERNSTEIN, P.L.C.
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P21955.A02

**APPENDIX
MARKED-UP COPY OF CHANGES TO CLAIMS**

3. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 and 2] claim 1, where the specific BET surface area is from 0.5 to 1.9 m²/g.

4. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 and 2] claim 1, where the specific BET surface area is from 0.6 to 1.5 m²/g.

5. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 to 4] claim 1, where the particle size, determined from the d₅₀ value, is greater than 1 μm.

6. (Amended) A lithium intercalation compound having a spinel structure and containing lithium manganese oxide as claimed in [claims 1 to 5] claim 1, where the diameter, determined from the d₉₀ value, is less than 25 μm.

7. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 to 5] claim 1, where the diameter, determined from the d₉₀ value, is less than 20 μm.

11. (Amended) A process for the preparation of a lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 8 to 10] claim 8, where the particulate, crystalline spinel precursor compound consists of the three phases MnO, LiMnO₂ and Mn₃O₄.

P21955.A02

14. (Amended) A process as claimed in [one of claims 8 to 13] claim 8, where, after the heating in an oxidizing atmosphere, the resultant solid is suspended in water with addition of one or more alkaline lithium compounds, and the suspension is spray-dried at a temperature of from 100°C to 400°C.

16. (Amended) A process as claimed in [one of claims 8 to 15] claim 8, where the intimate mixing is carried out in the presence of a sintering aid in a concentration of from 0.1 to 3%, based on the weight of the solids employed.

Lithium intercalation compounds containing lithium,
manganese oxide

Description

5

The invention relates to improved lithium intercalation compounds containing lithium manganese oxide and having a spinel structure for thin-film electrodes, to a process for their preparation, to electrodes produced therefrom, and to secondary lithium ion batteries containing lithium intercalation compounds containing lithium manganese oxide as active material of the positive electrode.

15 Lithium ion batteries can be made from one or more electrochemical cells which contain electrochemically active pigments. Cells of this type typically consist of an anode (negative electrode), a separator, a cathode (positive electrode) and an electrolyte.

20 Batteries containing metallic lithium as anode are known, as are those containing graphite, coke or other carbon particles which, as is known, are able to intercalate alkali metal ions. Also known are batteries containing other lithium intercalation compounds, i.e.

25 substances which are able to incorporate and release lithium under the action of an electric potential. The electrolyte typically consists of a lithium salt dissolved in one or more aprotic, normally organic solvents. Further suitable electrolytes are solid

30 electrolytes which consist of a polymeric matrix containing an ionically conductive, but electronically insulating medium. The charging process is generally defined in such a way that the anode (the negative pole) takes up lithium ions during charging, while the

35 cathode (the positive pole) serves as a source of lithium ions. Cells containing lithium metal as anode are usually charged during assembly.

Cells with anodes containing graphite or other carbon or another host substance which is capable of taking up lithium ions are usually uncharged during assembly. In order that they can be used as energy stores, they must be connected and charged against an intercalation compound containing lithium ions, preferably an intercalation compound containing lithium oxide. During charging, the lithium ions migrate from the intercalation compound to the graphite or carbon or another host substance which is capable of taking up lithium ions. The cell can then be discharged again, during which the lithium moves back. Rechargeable batteries of this type which do not contain metallic lithium are known as lithium ion batteries. Examples thereof are described in US 4,464,447 and US 5,418,090.

LiCoO_2 , LiMn_2O_4 and LiNiO_2 are preferably employed as oxidic materials in the cathodes. All these compounds are also employed with varied mixing ratios of the metal ions in order to establish certain advantages in charging or in the service life. Some or all of the oxygen is sometimes replaced by other elements, for example fluorine or sulfur. While the cobalt compounds are expensive, the nickel compounds are difficult to prepare. By contrast, manganese compounds are relatively cheap.

The specific charge of LiMn_2O_4 is theoretically 148 milliampere hours per gram. This value can be changed by varying the oxygen content or the ratio between the lithium and the manganese. In the opinion of many experts, however, LiMn_2O_4 can only reversibly cycle about 110-120 milliampere hours per gram, corresponding to about 0.8 mol of lithium per formula unit, in the long term. In the case of LiNiO_2 and LiCoO_2 , only about 0.5 mol of lithium per formula unit can be reversibly

5

20

- 35

A wet-chemical process for the preparation of a lithium manganese oxide spinel is described in DE 19 515 629. Here, a lithium compound and a manganese salt are
5 reacted in the disperse phase and dried, after which the dry residue is subjected to a sequence of grinding and heating steps. A further wet-chemical synthetic process is described in US 5,742,070. It is essentially based on the preparation of solutions of lithium,
10 transition metal and organic acids and alcohols, which are subsequently dried, ground and heated.

PCT Application WO 97/37935 claims a dry preparation process in which mixtures of manganese oxides and
15 lithium compounds, each with a controlled particle size distribution, are repeatedly heated at selected temperatures. PCT application WO 98/02931 describes a process for the preparation of lithium manganese intercalation oxides which consists of the reaction of LiOH,
20 MnO₂ and at least one polyfunctional alcohol followed by heat treatment. However, the known preparation processes for lithium manganese oxide pigments require either expensive raw materials, such as readily soluble manganese compounds, or complex process steps in order
25 to meet the high demands made of lithium manganese oxide pigments for use in electrodes. In particular, no suitable process was known for the preparation of smooth lithium manganese oxide pigments which are suitable for use in particularly thin-layered
30 electrodes.

The present invention therefore had the object of providing lithium manganese oxide intercalation compounds having a spinel structure and having a high
35 specific charge density which are suitable for use in particularly thin-layered electrodes for high-performance secondary lithium ion batteries. A further

number of lithium atoms, and heating at from 600°C to 1000°C in a non-oxidizing atmosphere, followed by grinding, giving a particulate, crystalline spinel precursor compound;

5

- b) heating the crystalline spinel precursor compound in an oxidizing atmosphere at from 500°C to 800°C with a residence time of from 0.5 to 10 hours.

- 10 It has also been found that thin-film electrodes which contain lithium manganese oxide intercalation compounds having a spinel structure prepared by the process according to the invention achieve a high specific charge density and high performance in secondary
15 lithium ion batteries. Thin-film electrodes of this type are produced by general processes which are known per se, for example by spraying, knife coating and pressing of mixtures of the lithium manganese oxide intercalation compound according to the invention,
20 conductive pigment and binder, if desired as a mixture with suitable solvents and further additives, onto a metallic, electrically conducting, thin foil or another suitable collector.
- 25 It has furthermore been found that secondary lithium ion batteries which contain the lithium manganese oxide intercalation compounds according to the invention as active material of the positive electrode have high performance and at the same time are inexpensive to
30 produce, are safe and are environmentally friendly.

Secondary lithium ion batteries of this type are produced in a manner known per se and essentially consist of a positive electrode, a negative electrode,
35 a separator and an electrolyte in a casing. For the secondary lithium ion batteries according to the invention, the lithium manganese oxide intercalation

compounds according to the invention are used as active material with a suitable binder known per se in the positive electrode, while the active material employed for the negative electrode is graphite or carbon or
5 another host substance which is capable of taking up lithium ions, with a suitable binder known per se.

The lithium manganese oxide intercalation compounds having a spinel structure according to the invention
10 are distinguished by particularly good processing and electrical properties. They are suitable for use in particularly thin-layered electrodes. The specific surface area of the lithium manganese oxide intercalation compounds according to the invention is
15 in the range $0.3 - 5 \text{ m}^2/\text{g}$, preferably $0.5 - 1.9 \text{ m}^2/\text{g}$ and very preferably $0.6 - 1.5 \text{ m}^2/\text{g}$. The particle size, measured from the d_{50} value, is greater than $0.5 \text{ }\mu\text{m}$, preferably greater than $1 \text{ }\mu\text{m}$. The diameter of the particles is advantageously not greater than $d_{90} =$
20 $30 \text{ }\mu\text{m}$, preferably less than $d_{90} = 25 \text{ }\mu\text{m}$, very preferably less than $d_{90} = 20 \text{ }\mu\text{m}$. The particles are essentially free from internal pores. Internal pores are defined as follows: the size of the internal pores d_{internal} depends on the particle size d_{50} . Internal pores are always the
25 same size as or smaller than a quarter of the particle size d_{50} and are of equal size or larger than $0.01 \text{ }\mu\text{m}$. The following correlation thus arises for the size range of the internal pores:

30 $0.01 \text{ }\mu\text{m} \leq d_{\text{internal}} \leq d_{50}/4.$

The internal pore volume is the cumulative pore volume of pores in this size range. The lithium manganese oxide particles according to the invention are
35 particularly smooth and have a low internal pore volume of less than 0.05 ml/g and preferably less than 0.03 ml/g .

In addition, the lithium manganese oxide intercalation compounds according to the invention are very crystalline, which is evident from very sharp diffraction reflections in the diffractograms. Sharp diffraction reflections are generally formed in the case of large crystallite sizes.

The process according to the invention for the preparation of lithium manganese oxide intercalation compounds having a spinel structure consists at least of two steps:

- I. the preparation of a particulate, crystalline precursor compound by intimate mixing of the starting materials, heating in a non-oxidizing atmosphere and subsequent grinding;
- II. heating in an oxidizing atmosphere, in which the particulate, crystalline spinel precursor compound is converted into the smooth, highly crystalline lithium manganese oxide intercalation compound having a spinel structure according to the invention.

The synthesis of a lithium manganese oxide having the morphology according to the invention by the process according to the invention is described below:

- 1.1. Mixing of the starting materials Li_2CO_3 and manganese oxide Mn_2O_3 . Suitable starting materials for the preparation of the lithium manganese oxide according to the invention are also various other known manganese and lithium compounds, for example Li_2O_2 , Mn_2O_3 or MnO_2 , or mixtures of lithium oxides or manganese oxides, so long as the mixture contains sufficient active oxygen. The preferred

- 1.3. Grinding of the heated mixture until a finely divided mixture is obtained. Suitable mills here are, for example, tin mills, impact disk mills, universal mills, jet mills or the like, optionally with classification. It is also possible to carry out a plurality of grinding processes one after the other in identical or different mills.
- 1.4. Optional additional step: reheating as in point 1.2, where the temperature may be the same as or higher than in point 1.2, but is not higher than 1000°C and is preferably not higher than 950°C. The residence time is likewise from 15 to 120 minutes.
- 1.5. Optional additional step: regrinding as in point 1.3, where the same or a different mill as in 1.3 can be selected and particle sizes and particle size distributions the same as or different from 1.3 are achieved.
2. Heating of the particulate, crystalline spinel precursor compound under an oxidizing atmosphere at 500°C - 800°C with a residence time of from 0.5 to 10 hours. The heating here can be carried out in a rotary tube furnace, preferably at from 700°C to 800°C and - if the furnace is fitted with a plurality of heating zones - at a reduced temperature of 450°C - 750°C in the final heating zone. The residence time in the heating zone is preferably 0.5 - 6 hours. The oxidizing atmosphere is preferably produced with oxygen. The heating can likewise be carried out in a stationary furnace under an oxidizing atmosphere at a preferred temperature of from 650°C to 750°C with a residence time of preferably greater than 5

hours. Here too, the oxidizing atmosphere is preferably produced with oxygen.

3. Optional addition step: suspension of the lithium
5 manganese oxide intercalation compound having a
spinel structure in water with addition of one or
more alkaline lithium salts, followed by spray-
drying at temperatures of from 100°C to 400°C.
Suitable alkaline aluminum salts are, for example,
10 Li_2CO_3 , Li_2O_2 , LiNO_3 , LiOH or mixtures of two or
more thereof. Preference is given to Li_2CO_3 . The
spray-drying may be followed by post-drying at
temperatures of from 100°C to 300°C.

- 15 In order to simplify the sintering, a sintering aid can
be added in steps 1.1 to 2 in a concentration of from
0.1 to 3% by weight, based on the solids content. The
sintering aid is preferably added during preparation of
the mixture, step 1.1. The sintering aid employed is
20 preferably a boron oxide, particularly preferably H_3BO_3 .

Thin-film electrodes which contain the lithium
manganese oxide compounds prepared by the process
according to the invention can be produced as follows:

- 25 A mixture of the pigment according to the invention,
conductive black having a surface area of greater than
50 m^2/g , graphite and a fluorine-containing binder, as
well as volatile solvents, such as, for example,
30 N-methylpyrrolidone (NMP) and/or acetone, is prepared.
The following amounts are generally employed: pigment:
80 parts by weight, conductive black and graphite:
5 - 15 parts by weight, binder: 5 - 15 parts by weight.
The amount of solvent is selected in such a way that
35 the mixture can be sprayed, cast or knife-coated.

The mixture is applied to an electrically conductive collector in one or more operations, and the solvent is evaporated. The applied layer can be sealed by known methods, such as rolling or pressing.

5

In order to produce a secondary lithium ion battery, a thin-film electrode produced by the process described above is used as cathode, while the anode employed is a lithium metal electrode or a thin-film electrode consisting of graphite, carbon or another material which is capable of taking up lithium electrons, and a suitable binder. These electrodes are assembled together with a separator and an electrolyte and optionally further constituents in a casing to give a secondary battery and charged. Secondary lithium ion batteries produced in this way have excellent service properties.

The lithium manganese oxide intercalation compounds prepared by the process according to the invention have the morphology described in claim 1. They can advantageously be used for the production of particularly thin thin-film electrodes. Secondary lithium ion batteries which contain the lithium manganese oxide spinels according to the invention as active material of the positive electrode are particularly suitable as high-performance batteries.

The invention is described below in greater detail with reference to figures 1 to 3 and an example, but is not restricted thereto.

Fig. 1 shows the size range of the internal pores and the internal pore volume for an Li/Mn spinel in accordance with the example according to the invention

Fig. 2 shows the size range of the internal pores and the internal pore volume of a commercially available Li/Mn spinel having a specific surface area of $1.2 \text{ m}^2/\text{g}$

5

Fig. 3 shows the X-ray diffraction pattern of the spinel precursor compound in accordance with the present invention

10 Example according to the invention: Preparation of an Li/Mn spinel

1.1 Mixing

15 712 kg of manganese oxide (Mn_3O_4 from Fermac, Ludwigshafen, after grinding in an Alpine 250 Z pin mill) and 184.5 kg of lithium carbonate (product ground to less than $40 \mu\text{m}$ from Chemetall, Frankfurt) are mixed for 30 minutes in a drum mixer with 3 knife heads
20 (capacity 2 m^3 , Lödige). The following measurement values were obtained from the mixture: bulk density: 0.7 g/ml , tamped density: 1.3 g/ml , specific surface area: $12 \text{ m}^2/\text{g}$.

1.2. and 1.3. Heating under N_2 and grinding

25

The mixture from 1.1 was heated in a gas-heated rotary tube furnace (Elino, length of heating zone 3.2 m , diameter 300 mm). The firing temperature was $750 \pm 10^\circ\text{C}$. 11 m^3 of nitrogen per hour were passed in
30 cocurrent through the tube. The furnace atmosphere was protected against the ambient air by a double flap airlock valve at the tube end, so that the oxygen content in the rotary tube dropped below 1%. The mixture was metered into the tube at about
35 $30 - 40 \text{ kg/h}$. The tube rotated at 2 revolutions per minute. The inclination of the tube was 0.5° , so that the residence time of the product in the heating

zone was about 1 hour. A preliminary fraction of a few kilograms of product was discarded. 500 kg of fired product were subsequently collected. The product was ground in a pin mill (Alpine 250 Z). The following measurement values were obtained: bulk density: 0.8 g/ml, tamped density: 1.0 g/ml, specific surface area: 3 m²/g. About 6 hours after commencement of the synthesis, a sample was taken from the tube outlet and analyzed by X-rays. Numerous sharp diffraction reflections were found (see Figure 3), which indicate the presence of the following crystalline phases: LiMnO₂ (35-0749), MnO (7-0230) and Mn₃O₄ (24-0734). No spinel phase was observed. The numbers shown in brackets indicate the assignment of the diffraction reflections to the compounds in the JCPDS file. The carbon content of the sample was 0.39 percent by weight, which indicated substantially complete decomposition of the Li₂CO₃ employed, i.e. to less than 0.4%.

20

1.4 and 1.5. Heating under N₂ and grinding

The ground fired product from 1.3 was reheated in the gas-heated rotary tube furnace (see above). The firing temperature was 825°C. 10 ± 1 m³/h of nitrogen were passed in cocurrent through the tube. The furnace atmosphere was protected against the ambient air by a double flap airlock valve at the tube end, so that the oxygen content in the rotary tube was less than 1%. The mixture was metered into the tube at about 25 kg/h. The tube rotated at 2 revolutions per minute. The inclination of the tube was 0.5 degree, so that the residence time of the product in the heating zone was about 1 hour. A preliminary fraction of a few kilograms of product was discarded. 169.5 kg of fired product were subsequently collected. The product was ground in a pin mill (Alpine 250 Z). The following measurement

values were obtained: bulk density: 0.8 g/ml, tamped density: 1.4 g/ml, specific surface area: 1.1 m²/g.

1.5.1. Repetition of the grinding

5 Since the product from 1.5 still contained slightly scratching components, the grinding of a part quantity of 54 kg was repeated in a mill with classifier wheel (Alpine ZPS 50). The mill rotor speed was 15,000 rpm, and the classifier wheel rotated at 4000 rpm. The following measurement values of the classifier-ground product were obtained: bulk density: 1.0 g/ml, tamped density: 1.3 g/ml, specific surface area: 1.4 m²/g. The particle size distribution was as follows: d₁₀ = 1.0 μm, d₅₀ = 3.0 μm, d₉₀ = 14 μm.

2. Heating under an oxidizing atmosphere

An amount of 40 kg of the ground fired product from 1.5.1 was heated in an electrically heated rotary tube furnace. The powder was metered into the tube at about 5.4 kg/h. The firing temperature was 775°C (length of the heating zone 140 cm). 0.6 m³ per hour of oxygen was passed in cocurrent through the tube (diameter 25 cm). The tube rotated at 4/3 rotations per minute and was paused for 1 minute every quarter rotation so that the residence time of the product in the heating zone reached about 3.3 hours. The inclination of the tube was 0.25 degree. 28.9 kg of lithium manganese oxide spinel were prepared. The following measurement values were obtained: bulk density: 1.0 g/ml, tamped density: 1.1 g/ml, specific surface area: 0.7 m²/g, pH: 8.5, particle size distribution: d₁₀ = 2.7 μm, d₅₀ = 7 μm, d₉₀ = 23 μm. The X-ray diffraction analysis showed the diffractogram of a phase-pure Li/Mn spinel (analogous to JCPDS 35-0782) and gave a crystallite size of 0.5 μm, evident from sharp diffraction reflections, some of

which were split even at 36 degrees. The power charge was determined, and a value of 108 Ah/kg was found in the 5th discharge (lithium intercalation).

5 3. Suspension and spray-drying with Li_2CO_3

A suspension of 10 kg of the fired product from 2., 10 liters of water and 100 g of lithium carbonate was stirred in a tank using a Kotthof dispersion unit and
10 dried in a spray drier (Niro Minor) using an atomization wheel. The heating-gas temperature was $350 \pm 5^\circ\text{C}$, and the outlet gas temperature was $130 \pm 5^\circ\text{C}$. The atomizer gas pressure was 4.6 bar. 8.9 kg of Li/Mn spinel having an Li_2CO_3 layer were obtained. The
15 particle size distribution was as follows: $d_{10} = 2.3 \mu\text{m}$, $d_{50} = 5 \mu\text{m}$, $d_{90} = 15 \mu\text{m}$, specific surface area: $0.9 \text{ m}^2/\text{g}$. Finally, the powder was dried at 110°C for 1 hour in a vacuum drying cabinet (water-jet vacuum).

20 In addition, the pore size distribution was determined using the mercury porosymmetry method. Interpores (i.e. pores between particles which were not connected to one another) having a size of 1 - 4 μm were evident. The incremental intrusion volume reached a local maximum of
25 0.045 ml/g at a pore size of 3 μm . No pores were observed in the range from 0.02 to 1 μm . The powder charge data were determined, and a value of 106 Ah/kg was found in the 5th discharge.

30 Analytical measurements:

1. Pore size distribution:

The pore size distribution in the pore size range
35 between 0.01 and 100 μm was determined using the mercury porosymmetry method with an Autopore II instrument (in accordance with DIN 66133). Using this

method, internal pores, i.e. the pores within coherent particles and the pores arising from the surface roughness, and interpores, i.e. the pores between different particles which are not connected to one another, can be measured. Pores larger than 50 μm arising from the loose bed of a powder are also measured.

2. Specific surface area:

10

The specific surface area (BET) was determined using a Ströhlein Areameter from Ströhlein, Düsseldorf, by the one-point difference method of Haul and Dümbgen in accordance with DIN 66131. The pigments were dried at 140°C for at least 12 hours.

3. X-ray diffractograms:

X-ray diffractograms were obtained using the AXS D5000 diffractometer. The crystallite size was calculated from the integral half-value width of the 311 peak using the Debye Scherrer formula and taking into account the usual correction for the apparatus spread.

4. Particle size distribution:

The particle size distribution was determined by laser diffraction in a SYMPATEC HELOS instrument. In this measurement, a spatula tip of the powder to be analyzed was added to the circulating water bath (optical concentration: about 15 - 50%). The particles were distributed by ultrasound for 50 seconds before and during the measurement, which took 10 seconds. This measurement essentially determined the diameter of the coherent agglomerates.

5. Powder charge data:

The powder charge data were determined as follows:

5 Firstly, auxiliaries were mixed in a mill: 1 g of carbon black (for example Vulcan XC-72 or Ensaco 250) plus 1 g of graphite (SFG 10) plus 2.2 g of PVDF (Aldrich). A coating comprising 2 g of spinel and 0.4 g of auxiliaries in NMP (N-methylpyrrolidone) was stirred using a high-speed stirrer. In order to produce the layer to be tested, the coating was sprayed onto the titanium collector, which had in each case been predried and slightly warmed, in up to four repetitions. The area of the current collector was 1.3 cm². Between each application, the coating was homogenized using the high-speed stirrer and immediately processed further in order to counter possible separation of the solids. The coating was sprayed onto the prewarmed titanium collector with the aid of a spray gun (air brush spray gun) and dried. The most critical step for the reproducibility and correctness of the measurement was the weighing of the dried layer on the Ti collector. The layer weighed about 25 mg; it was weighed to a resolution of 0.1 mg, corresponding to an error of 0.4%, in the case of differential weighing a maximum of 0.8%, but on average less.

30 The electrodes were dried for at least 12 hours at 120°C in an oil-pump vacuum before they were assembled into an electrochemical cell in a glove box filled with argon. The anode used was lithium metal (Aldrich, 99.9%, 0.75 mm thickness), and the commercially available electrolyte solution LP 30 (1M LiPF₆ in ethylene carbonate/dimethyl carbonate 1:1, Merck) was furthermore used. The separator was a glass nonwoven with a thickness of about 2 mm. The geometry of the charge measurement cells is described in P. Novák,

W. Scheifele, F. Joho, O. Haas, *J. Electrochem. Soc.*
142, 2544 (1995), see there in particular figure 1
(although the reference electrode shown there was not
used).

5

The charging and discharging were carried out in the
potential range between 3.3 and 4.4 volts with constant
currents of 10 μ A per milligram of oxide, which
resulted in charging and discharging times in the order
10 of greater than 10 hours in each case.

6. Method for determination of the pore volume

The pore volume was determined as follows: the pore
15 size distribution in the pore size range between 0.01
and 100 μ m was determined using the mercury
porosymmetry method with an Autopore II instrument (in
accordance with DIN 66133).

Patent Claims:

1. A lithium intercalation compound containing lithium manganese oxide and having a spinel structure for thin-film electrodes, where the lithium intercalation compound has
- a specific surface area, determined by the BET method, of from 0.3 to 5 m²/g,
 - a particle size, determined from the d₅₀ value, of greater than 0.5 μm,
 - a diameter, determined from the d₉₀ value, of 30 μm or less, and an internal pore volume of less than 0.05 ml/g and has a pronounced crystal structure.
2. A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claim 1, where the internal pore volume is less than 0.03 ml/g.
3. A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claims 1 and 2, where the specific BET surface area is from 0.5 to 1.9 m²/g.
4. A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claims 1 and 2, where the specific BET surface area is from 0.6 to 1.5 m²/g.
5. A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claims 1 to 4, where the

particle size, determined from the d_{50} value, is greater than 1 μm .

- 5 6. A lithium intercalation compound having a spinel structure and containing lithium manganese oxide as claimed in claims 1 to 5, where the diameter, determined from the d_{90} value, is less than 25 μm .
- 10 7. A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claims 1 to 5, where the diameter, determined from the d_{90} value, is less than 20 μm .
- 15 8. A process for the preparation of a lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claim 1, by
- 20 a) preparation of an intimate mixture of one or more lithium compounds and one or more manganese compounds, where at least one of these compounds or the sum of all compounds contains sufficient active oxygen that the
- 25 number of equivalents of active oxygen is equal to or greater than the number of lithium atoms, and heating at from 600°C to 1000°C in a non-oxidizing atmosphere, followed by grinding, giving a particulate,
- 30 crystalline spinel precursor compound;
- b) heating the crystalline spinel precursor compound in an oxidizing atmosphere at from 500°C to 800°C with a residence time of from
- 35 0.5 to 10 hours.

9. A process for the preparation of a lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claim 1, by
- 5
- a) a1) preparation of an intimate mixture of Li_2O_3 and Mn_3O_4 ,
- 10 a2) heating at from 600°C to 1000°C under nitrogen, argon or another non-oxidizing atmosphere with a residence time of from 15 to 120 minutes in a rotary tube furnace,
- 15 a3) grinding the heated mixture to give a particulate, crystalline precursor compound;
- 20 b) heating of the spinel precursor compound in an oxidizing atmosphere at from 500°C to 800°C with a residence time of from 0.5 to 10 hours.
- 25 10. A process for the preparation of a lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claim 9, where the heating in a2) and grinding in a3) are carried out two or more times.
- 30 11. A process for the preparation of a lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claims 8 to 10, where the particulate, crystalline spinel precursor compound consists of the three
- 35 phases MnO , LiMnO_2 and Mn_3O_4 .

12. A process for the preparation of a lithium inter-
calation compound containing lithium manganese
oxide and having a spinel structure as claimed in
claim 9, where the heating in an oxidizing
atmosphere is carried out in a rotary tube furnace
at a temperature of from 700°C to 800°C with a
residence time of from 0.5 to 6 hours.
13. A process for the preparation of a lithium inter-
calation compound containing lithium manganese
oxide and having a spinel structure as claimed in
claim 9, where the heating in an oxidizing
atmosphere is carried out in a stationary furnace
at a temperature of from 650°C to 750°C with a
residence time of greater than 5 hours.
14. A process as claimed in one of claims 8 to 13,
where, after the heating in an oxidizing
atmosphere, the resultant solid is suspended in
water with addition of one or more alkaline
lithium compounds, and the suspension is spray-
dried at a temperature of from 100°C to 400°C.
15. A process as claimed in claim 14, where the
alkaline lithium compound is Li_2CO_3 , Li_2O_2 , LiNO_3 ,
 LiOH or a mixture of two or more of these
compounds.
16. A process as claimed in one of claims 8 to 15,
where the intimate mixing is carried out in the
presence of a sintering aid in a concentration of
from 0.1 to 3%, based on the weight of the solids
employed.
17. A process as claimed in claim 16, where the
sintering aid is a boron oxide.

18. A process as claimed in claim 17, where the boron oxide is H_3BO_3 .
19. A thin-film electrode for secondary lithium ion batteries containing lithium manganese oxide as claimed in claim 1 as the active material.
20. A secondary lithium ion battery containing lithium manganese oxide as claimed in claim 1 as the active material of the positive electrode.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
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TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

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sisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI,
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(BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE,
SN, TD, TG).

Veröffentlicht:

- Mit internationalem Recherchenbericht.
- Vor Ablauf der für Änderungen der Ansprüche geltenden
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Zur Erklärung der Zweibuchstaben-Codes, und der anderen
Abkürzungen wird auf die Erklärungen ("Guidance Notes on
Codes and Abbreviations") am Anfang jeder regulären Ausgabe
der PCT-Gazette verwiesen.

(54) Title: LITHIUM INTERCALATION COMPOUNDS CONTAINING LITHIUM MANGANESE OXIDE

(54) Bezeichnung: LITHIUMMANGANOXID ENTHALTENDE LITHIUMINTERKALATIONSVERBINDUNGEN

(57) Abstract: The invention relates to improved lithium intercalation compounds containing lithium manganese oxide, having a spinell structure and a special morphology for thin-film electrodes. The invention further relates to a method for the production of said compounds, electrodes produced from said compounds and secondary lithium batteries with lithium intercalation compounds containing lithium manganese oxide as an active material for the positive electrode, offering high energy and able to be produced in an inexpensive manner in addition to being ecologically friendly and safe.

(57) Zusammenfassung: Die Erfindung betrifft verbesserte, Lithiummanganoxid enthaltende Lithiuminterkalationsverbindungen mit Spinellstruktur und besonderer Morphologie für Dünnschichtelektroden, ein Verfahren zu deren Herstellung, daraus hergestellte Elektroden sowie sekundäre Lithiumionenbatterien mit Lithiummanganoxid enthaltenden Lithiuminterkalationsverbindungen als aktives Material der positiven Elektrode, die eine hohe Leistung aufweisen und preisgünstig herstellbar, umweltfreundlich und sicher sind.

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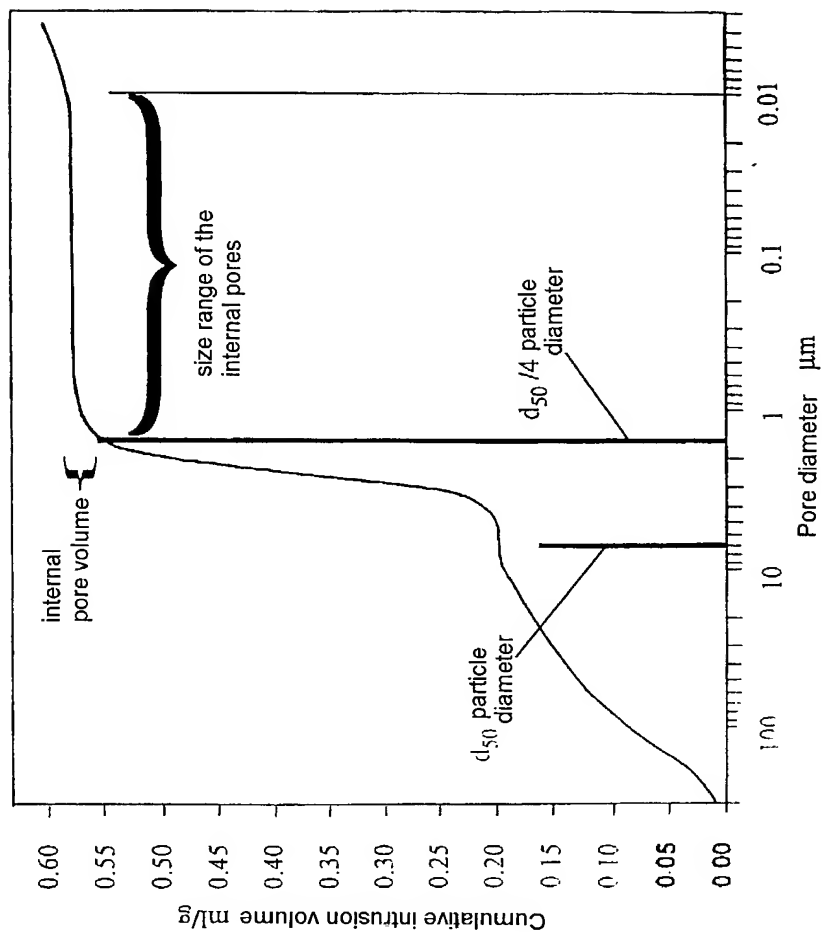


Fig 1

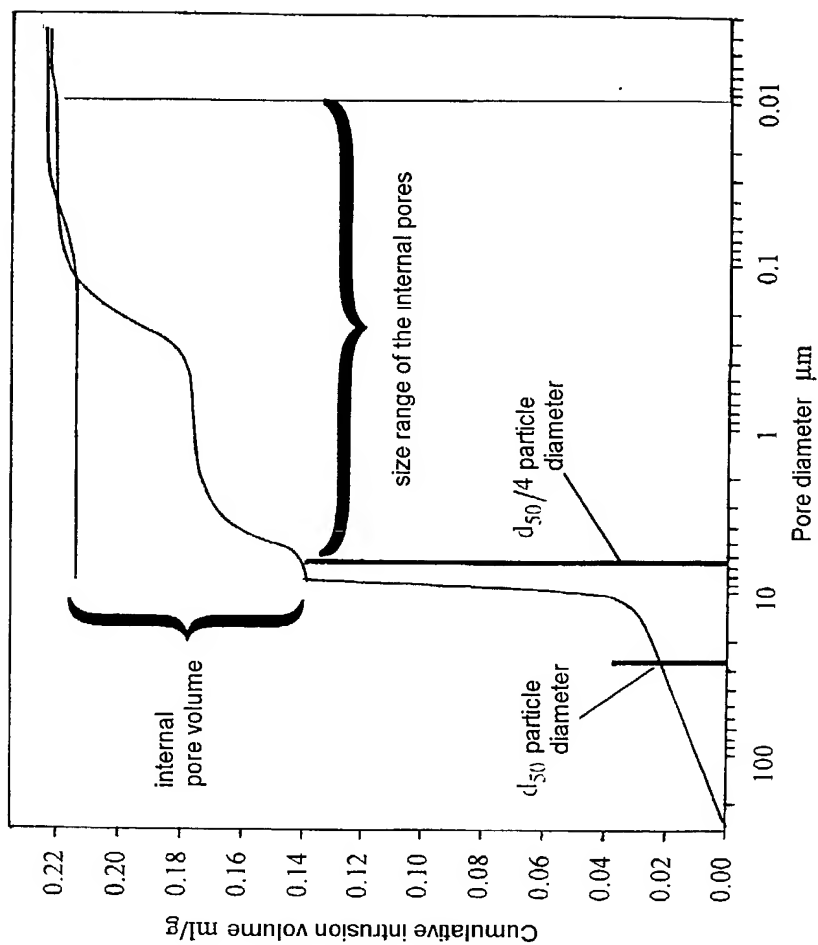


Fig. 2

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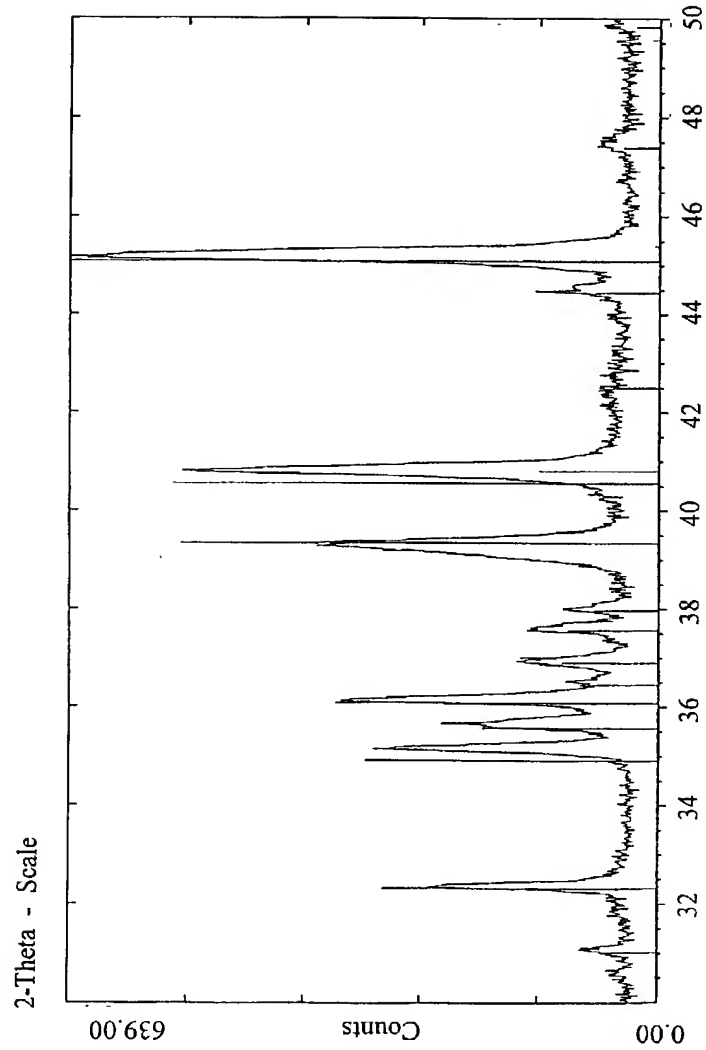


Fig. 3

Declaration and Power of Attorney For Utility or Design Patent Application

Erklärung für Patentanmeldungen zur Gebrauchseignung und Entwicklung
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German Language Declaration

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LITHIUMMANGANOXID ENTHALTENDE
LITHIUMINTERKALATIONSVERBINDUNGEN

deren Beschreibung hier beigelegt ist, es sei denn (in diesem Falle
Zutreffendes bitte ankreuzen), diese Erfindung

☒ wurde angemeldet am 15 juli 2000
unter der US-Anmeldenummer 10/031,933
und wurde am _____ abgeändert (falls zutreffend)
oder

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Prior Foreign Applications
Frühere ausländische Anmeldungen

| | |
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| (Number) | (Country) |
| (Number) | (Land) |
| | |
| (Number) | (Country) |
| (Number) | (Land) |

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| <u>27 JULY 1999</u> |
| (Day/Month/Year Filed) |
| (Tag/Monat/Jahr der Anmeldung) |
| |
| (Day/Month/Year Filed) |
| (Tag/Monat/Jahr der Anmeldung) |

Priority Claimed
Prioritätsanspruch

| | |
|-------------------------------------|--------------------------|
| <input checked="" type="checkbox"/> | <input type="checkbox"/> |
| Yes | No |
| Ja | Nein |
| | |
| <input type="checkbox"/> | <input type="checkbox"/> |
| Yes | No |
| Ja | Nein |

☐ Zusätzliche einstweilige Anwendungsnummern sind im
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My residence, post office address and citizenship are as stated
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plural names are listed below) of the subject matter which is
claimed and for which a patent is sought on the invention entitled

LITHIUM INTERCALATION COMPOUNDS CONTAINING
LITHIUM MANGANESE OXIDE

the specification of which is attached hereto unless the following
box is checked:

☒ was filed on July 15, 2000 as
United States Application Number 10/031,933
and was amended on _____ (if applicable)
or,

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I acknowledge the duty to disclose information which is material
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| Wohnsitz | Residence |
| Staatsangehörigkeit | Citizenship |
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